Tetrahedron Letters No. 32, pp. 2741-2742, 1970. Pergamon Press. Printed in Great Britain.

Hexafluoroacetone-Hydrogen Peroxide, A New Peroxyacid

R.D. Chambers and M. Clark

Department of Chemistry, The University, South Road, Durham.

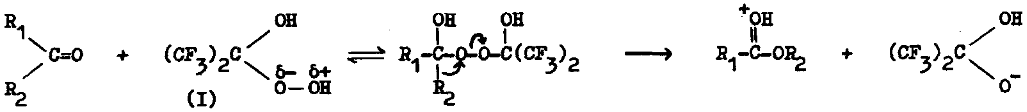
(Received in UK 2 June 1970; accepted for publication 11 June 1970)

The conversion of ketones to esters (Baeyer-Villiger reaction) is usually carried out with the more reactive peracids,[1] to avoid long reaction times etc. and the most effective peracid developed so far is trifluoroperoxyacetic acid. This reagent will also usually oxidize a primary aromatic amine to a nitro compound,[2] a reaction difficult to achieve with other reagents. The reactivity of trifluoroperoxyacetic acid is usually attributed to the polar nature of the oxygen-oxygen bond, arising from the influence of the trifluoromethyl group.

Hexafluoroacetone, now made on a commerical scale, forms a range of adducts with various donor molecules[3] and the hydrate is a strong acid.[4] We have now shown that a similar complex (I) is formed with hydrogen peroxide and since this adduct probably also has a highly polar oxygen-oxygen bond, we have investigated some reactions of (I) as an oxidizing agent. The results are summarized in the table.

Compound	Product	Yield %
Methyl isobutyl ketone	Isobutyl acetate	73
Methyl-n-amyl ketone	N-amyl acetate	81
Cyclohexanone	Caprolactone	50
Acetophenone	Phenyl acetate	34
Aniline	Nitrobenzene	65
Pentafluoroaniline	Decafluoroazobenzene	10
Mesitylene	Mesitol	40

Hydrogen peroxide is immiscible with methylene dichloride, but if hexafluoroacetone is absorbed into the rapidly stirred mixture from a vacuum system (or bubbled into the mixture) a single phase is obtained. Absorption of hexafluoroacetone occurs rapidly until approximately a 1:1 composition is obtained, and then further absorption will occur but at a significantly slower rate. The ketones were oxidized by addition to this mixture followed by a period at reflux (4-5 hrs.). Reaction with non-aromatic ketones occurs very cleanly to give high yields of the corresponding esters indicating that (I) does indeed function as a reactive peroxyacid.



Reactions with aromatic ketones are accompanied by tar formation which most probably results from electrophilic substitution in the aromatic ring.

Electrophilic hydroxylation of aromatic compounds is not common but occurs with trifluoroperoxyacetic acid,[5] particularly with added boron trifluoride[6] and reaction of (I) with mesitylene shows a similar reactivity giving mesitol although the addition of boron trifluoride had no beneficial effect in this case.

Aniline was oxidized smoothly, without reflux, to nitrobenzene but attempts to oxidize pentafluoroaniline gave only decafluoroazobenzene in low yield. A similar reaction using trifluoroperoxyacetic acid gave pentafluoronitrobenzene in high yield.[7]

Clearly then, the complex (I) is a very effective peroxyacid but these preliminary results suggest that it is less powerful than trifluoroperoxyacetic acid.

We thank Dr. R.D. Richardson and E.I. DuPont de Nemours and Co. for a gift of hexafluoroacetone, and S.R.C. for a maintenance grant (to M.C.).

1. H.O. House, "Modern Synthetic Reactions", W.A. Benjamin Inc., New York, 1965, p.123.
2. W.D. Emmons, J.Amer.Chem.Soc., 1954, 76, 3470; 1957, 79, 5528.
3. C.G. Krespan and W.J. Middleton, Fluorine Chem.Revs., 1967, 1, 145.
4. W.J. Middleton and R.V. Lindsey, J.Amer.Chem.Soc., 1964, 86, 4948.
5. R.D. Chambers, P. Goggin, and W.K.R. Musgrave, J. Chem. Soc., 1959, 1804.
6. H. Hart, C.A. Buehler, and A.J. Waring, A.C.S. Advances in Chemistry Series, No.51, 1965, pages 1-9.
7. G.M. Brooke, J. Burdon, and J.C. Tatlow, J. Chem. Soc., 1961, 802.